Indian J. Phys. **70A** (2), 259–264 (1996)

IJP A
— an international journal

Total binding energy *via* the band structure energy of 4*d* group transition metals

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Received 2 May 1995, accepted 6 November 1995

Abstract : The binding in metals provides a basis genesis to discuss the cohesive, elastic, lattice dynamical and other allied properties of the metals. A thorough and comprehensive analysis with regard to (i) various energy terms contributing to total metallic bonding, (ii) forms of the model potentials incurring the band structure part of the binding, (iii) implication of *s–d* hybridization and (iv) effect of electron screening, has prompted us to undertake the present study of binding in several complex metals which turn out to be superconducting at low temperatures and bear *hcp*, *bcc* and *fcc* configurations at room temperature *i.e.* Yttrium (Y), Zirconium (Zr), Niobium (Nb), Molybdenum (Mo), Ruthenium (Ru), Rhodium (Rh) and Palladium (Pd)

Keywords : Electron hopping, *s*- and *d*-bands, pseudopotential

PACS Nos. : 71.25.Pi, 71.45.Nt

Wills and Harrison [1] have dealt with the *s–s* interactions while Harrison and Froyen [2] have formulated the interactions implicating the *d*-band electrons. Chelikowsky [3] has calculated the binding energy of simple metals in Thomas-Fermi approximation. Empty core potential due to Heine and Abarenkov [4] has been deployed by Singh *et al* [5] while Wills and Harrison [1] have used a similar potential to calculate the binding in metals. These potentials [6] besides being discontinuous in real space, do not imbibe the short range repulsive character explicitly in their formulations.

Various interaction energies associated with the electrons are influenced by *s–d* hybridization which substantially alters the effective occupancy of metallic *d*- and *s*-states. The phenomenon of electron-screening also contributes to the binding of the metals.

The studies undertaken so far, involving pseudopotential theory [1–3,5], have used the fixed valence for the transition metals undertaken for the study, and fit the different

model radius parameter (s) to their model potential (s) to achieve the required purpose. The assignment of a chosen valence to particular transition metal may be questionable which led us to investigate the problem afresh with added thoroughness.

We have purposely treated this procedure for the transition metals just in a reverse manner to the conventional method *i.e.* leaving the valence Z as adjustable parameter and the model radius (s) as fixed (determined by fitting to the equilibrium volume) for all the metals.

Present study have utilized this approach for computing the binding energy in both real and Fourier space by taking the fixed model-radius for the metal. The appropriate valence (Z) corresponding to the metal, is then sought to get the corresponding value to the metalic experimental data.

Accordingly, the interaction system comprising of terms due to free electron gas, core, d-bands and band structure components, is carried out for the complex metals which exhibit superconducting properties at low temperature.

The binding energy comprises of four contributions [1] *i.e.* free electron energy (E_{fe}), d-band width energy (E_b), d-band center of gravity shift energy (E_c) and band structure energy (E_{bs}).

The bonding term due to the width of d-bands gives rise to attractive part of the energy. The shift of center of gravity of d-bands leads to a repulsive part of energy.

Following Wills and Harrison [1], Z_s for the metals is equated to 1.5 and the valence due to d-electrons *i.e.* $Z_d\ (= Z - Z_s)$ is determined by the knowledge of Z and Z_s.

The sum of above terms may now be written as

$$V_d = E_{fe} \quad E_b + E_c. \tag{1}$$

The input data needed to compute V_d for the metals under study are given in Table 1. The computed values of V_d for the metals are also shown in this table.

Table 1. Input data and computed $V(d)$ for the metals.

Metal	Lattice configuration	Lattice constant (Å)		Core radius (r_c) (Å)	d-state radius (r_d) (Å)	$V(d) = E_{fe} + E_b + E_c$ (ev / atom)
		a	c			
Y	*hcp*	3.65	3.75	1.09	1.58	-9.21331
Zr	*hcp*	3.23	5.15	1.06	1.41	-8.1536
Nb	*bcc*	3.30	—	1.01	1.28	-8.2022
Mo	*bcc*	3.15	—	0.95	1.20	-8.4820
Ru	*hcp*	2.71	4.28	0.72	1.05	-11.5329
Rh	*fcc*	3.80	—	0.62	0.99	-13.3734
Pd	*fcc*	3.89	—	0.52	0.94	-15.4489

To compute the band structure energy (E_{bs}) for the complex superconducting metals of present concern, we have made two-fold computations. To reveal the nature

of interactions in real space we have at first computed the energy at Fermi wave vector (k_f).

The expression for the band structure energy E^r_{bs} in real space may be written on the lines of Harrison [7] *i.e.*

$$E^r_{bs} = 9\pi Z_r^2/E_f \; W_b^2(2k_f) \cos(2k_f r_s)/(2k_f r_s)^3, \tag{2}$$

where E_f, k_f, r_s and W_b are the Fermi energy, Fermi radius, electron separation and bare ion form factor respectively [8–11]. The model potentials due to Ashcroft [8], Vrati *et al* [9], Idress *et al* [10] and Kulshrestha *et al* [11], are chosen to obtain the band structure energy.

In order to investigate the phenomenon of hybridization, the dependence of E^r_{bs} on Z_r is explored. The variation of E^r_{bs} with Z_r is depicted in Figure 1 for a representative

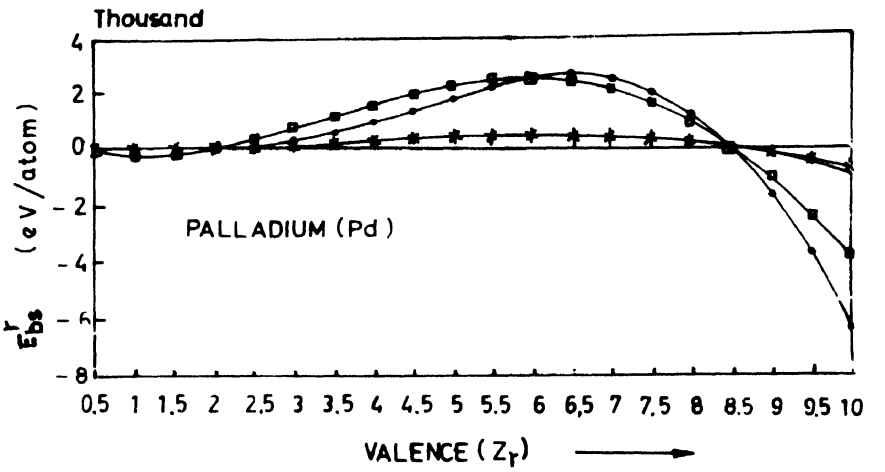

Figure 1. The dependence of band structure energy E^r_{bs} on valence Z_r for Pd, as a representative case, in real space. The symbols [+, *, ●, □], represent the computed findings for the Model potentials due to Ashcroft [8], Vrati *et al* [9], Idress *et al* [10] and Kulshrestha *et al* [11] respectively.

metal Pd. Relevant valence Z_r for which the E^r_{bs} assume the appropriately attractive character for different Model potentials are enlisted in Table 2.

For analyzing the characteristic features of interactions associated with the E^q_{bs}, we have further computed the band structure energy in Fourier space which may be expressed as

$$E^q_{bs} = \Omega/(4\pi e^2) \sum q^2 W_b^2(q) \, (\varepsilon(q)-1)/\left(1+\{(\varepsilon(q)-1)(1-f(q))\}\right), \tag{3}$$

where $\varepsilon(q)$ is the usual Hartree-Fock dielectric function, $f(q)$, the correction factor due to exchange and correlation effect associated with the electrons and $W_b(q)$, the bare ion form factors [8–11]. Present investigation employs an efficient and moderate scheme due to Vashishta and Singwi [12] for computing $f(q)$.

In order to study the process of *s–d* hybridization, the E_{bs}^{q} are computed for different Z_q. The computed plots E_{bs}^{q} *vs* Z_q within the frame work of the said potentials are shown in

Table 2. Total binding energy computed by using eq. (4).

Metal	References	Valence in *r*-space Z_r	Valence in *q*-space Z_f	Binding energy	
				Present	exp
Y	Ashcroft [8]	8.559	0.354	−17.122	−17.222
	Vrati *et al* [9]	8.550	0.640	−16.438	
	Idress *et al* [10]	8.537	0.122	−17.221	
	Kulshrestha *et al* [11]	—	—	—	
Zr	Ashcroft [8]	8.570	0.410	−19.568	−20.183
	Vrati *et al* [9]	8.562	0.747	−19.558	
	Idress *et al* [10]	8.542	0.141	−20.008	
	Kulshrestha *et al* [11]	8.544	0.150	−20.321	
Nb	Ashcroft [8]	8.561	0.415	−20.295	−21.337
	Vrati *et al* [9]	8.557	0.747	−21.033	
	Idress *et al* [10]	8.533	0.140	−21.171	
	Kulshrestha *et al* [11]	8.535	0.054	−20.566	
Mo	Ashcroft [8]	8.530	0.411	−21.785	−21.607
	Vrati *et al* [9]	8.521	0.730	−21.163	
	Idress *et al* [10]	8.496	0.138	−21.814	
	Kulshrestha *et al* [11]	8.500	0.200	−21.718	
Ru	Ashcroft [8]	8.545	0.355	−21.823	−21.97
	Vrati *et al* [9]	8.520	0.650	−21.668	
	Idress *et al* [10]	8.519	0.120	−21.943	
	Kulshrestha *et al* [11]	8.523	0.230	−22.082	
Rh	Ashcroft [8]	8.575	0.309	−21.549	−21.457
	Vrati *et al* [9]	8.572	0.546	−21.321	
	Idress *et al* [10]	8.558	0.103	−21.332	
	Kulshrestha *et al* [11]	8.559	0.295	−21.508	
Pd	Ashcroft [8]	8.529	0.270	−20.578	−21.240
	Vrati *et al* [9]	8.520	0.475	−21.038	
	Idress *et al* [10]	8.516	0.090	−21.069	
	Kulshrestha *et al* [11]	8.516	0.310	−21.508	

Figure 2 for the representative metal Pd. Table 2 exhibits some of the appropriate and attractive computed values of E_{bs}^{q} with the corresponding appropriate valence Z_q.

The total binding energy for the metallic ions of given valence and occupying the finite volume within the quoted model potentials treated in second order may be written as,

$$E_{\text{bind}} = V(d) + \left[E_{bs}^{r} + E_{bs}^{q}\right]/2. \tag{4}$$

For computing the binding energy in real space, we have substituted the E_{bs}^{r} at Z_r as per contents of the Table 2. The binding energy in Fourier space is computed by putting the E_{bs}^{q} at Z_q obtained from the data given in Table 2.

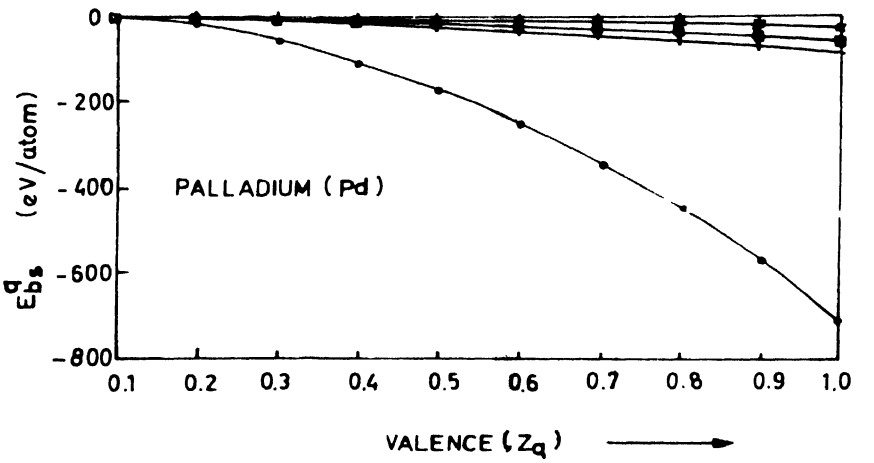

Figure 2. The dependence of Band structure energy E_{bs}^{q} on valence Z_q, Pd as a representative case, in Fourier space The symbols are present same as in Figure 1

The computed binding energy in real and Fourier spaces are enlisted in Table 2. The last row of the tables exhibits the experimental binding energy being computed by using the following relation,

$$E_{\text{bind}}\ (\text{Experimental}) = -E_{\text{cohesive}} - E_{\text{I}} - 1/4\ \left(E_{\text{I}} + E_{\text{II}}\right), \tag{5}$$

where E_{cohesive} is the cohesive energy, E_{I}, the first ionization energy and E_{II}, the second ionization energy. The E_{cohesive}, E_{I} and E_{II} data are taken from Kittel [13].

Present investigation accounts comprehensively for the contributions of almost all interactions present in the metals. The theory besides being extensive as compared to others [1,2], predicts good agreement with the experimental values.

The contents of Table 2 reveal that the accorded values of the binding energy are obtained for which the average values of the valences, Z_r and Z_q are 8.345 and 0.255 respectively. As the maximum occupancy number of the d and s subshells are 10 and 2 respectively, so in real space there may be much probability of transferring the electrons from $d \rightarrow s$ states while it is inverse, from $s \rightarrow d$, in Fourier space.

The study establishes that all the chosen model potentials irrespective of their shapes, forms and theoretical details lead to almost identical predictions of valence correlated band structure bonding.

The valence dependence of E_{bs}^{r} (Figure 1) exhibits one type of hybridization which suggests hopping of electrons from d-bands to s-bands. The E_{bs}^{q} *vs* Z_q (Figure 2) study reveals other type of hybridization which gives rise to the hopping from s-states to d-states.

The two types of hybridization associated with unscreened and screened electron-ion interactions points toward the inverse correlation between valence and shift of interaction energy due to the pseudopotential. The correlation may be attributed to the degree of oscillations of electron wave function occurring inside the core region.

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